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METHOD FOR PYROLYTIC DEPOSITION OF RESISTANCE FILMS

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2 Sheets-Sheet 1

Fig. 1.

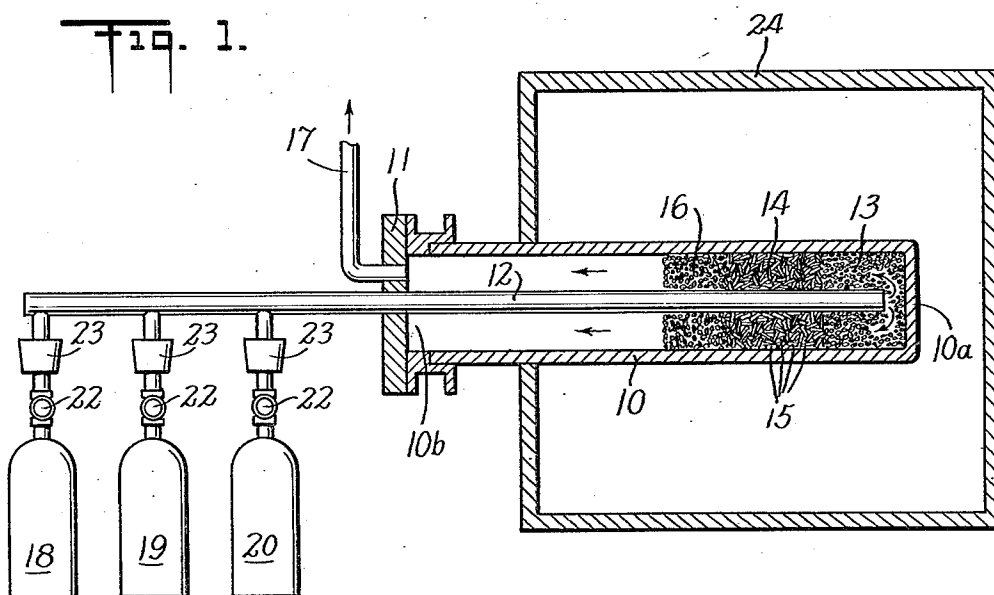


Fig. 2.



Fig. 3.

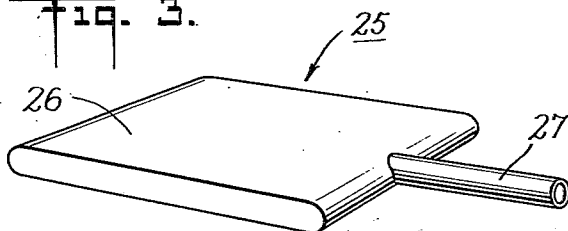


Fig. 4.

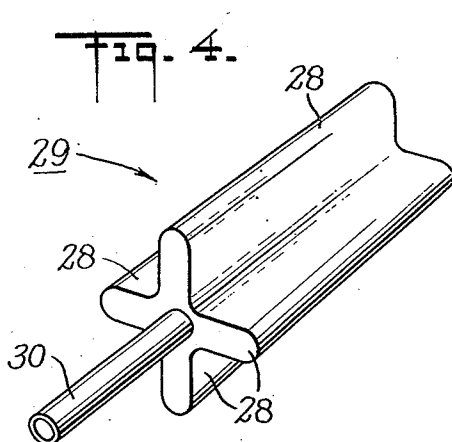
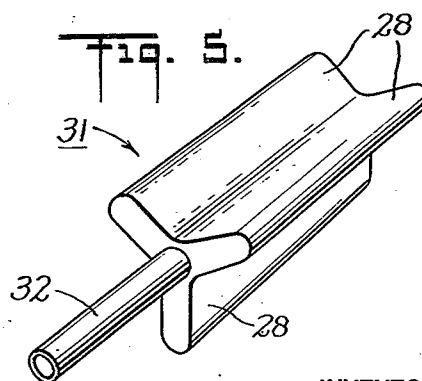


Fig. 5.



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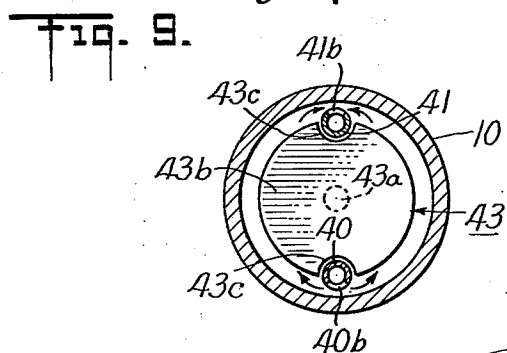
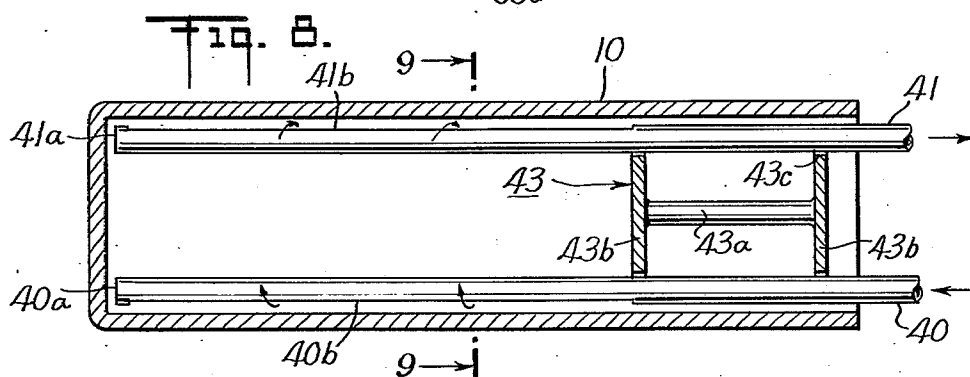
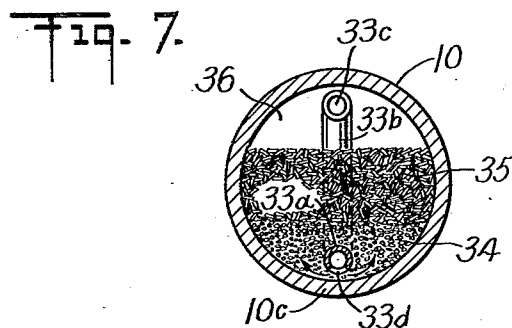
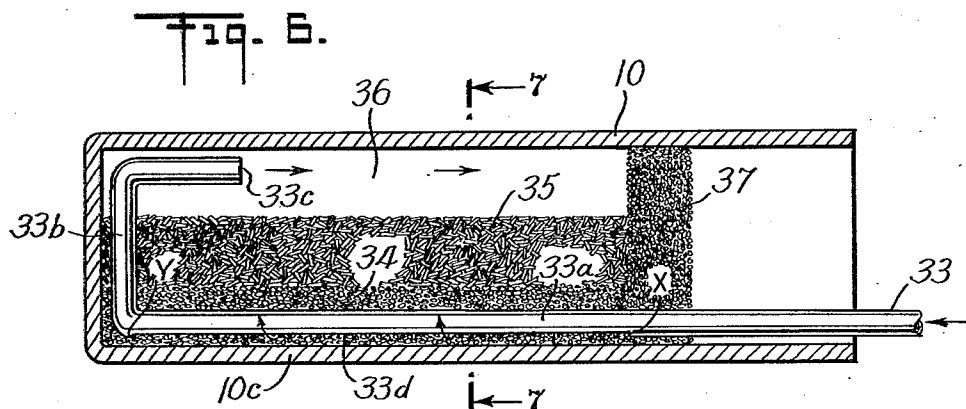
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METHOD FOR PYROLYTIC DEPOSITION OF RESISTANCE FILMS

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2 Sheets-Sheet 2



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**METHOD FOR PYROLYTIC DEPOSITION OF
RESISTANCE FILMS****Konrad Gentner, Warminster Township, Pa., assignor to
International Resistance Company, Philadelphia, Pa.****Application May 24, 1954, Serial No. 432,009****6 Claims. (Cl. 117—226)**

This invention relates to pyrolytic deposition of resistance material, such as carbon or carbon and boron, on a ceramic blank from a gas containing the desired deposition materials. More particularly, the invention is concerned with a method and apparatus for heating ceramic blanks in the presence of such gases to deposit a hard resistance coating on the blanks, which coating is unusually stable and free from impurities.

Resistors of this type are commonly known as "deposited carbon resistors" because of the method of applying the resistance coating by pyrolytic deposition. Such deposition is usually effected in a batch process in which a refractory flask is partially filled with ceramic blanks and heated. A hydrocarbon gas such as methane is passed through the flask after it has reached the deposition temperature of the gas, and, during deposition caused by cracking of the gases in the presence of the ceramics, the flask is rotated to expose all portions of the blanks to the gases. Accordingly, this method of pyrolytic deposition which has been standard practice in this art for some time depends on a flask having an interior considerably larger than the small batch of ceramic blanks constantly being agitated in a small pile as the flask rotates. The unfilled space in the flask must of necessity be filled with the carbon containing gas, such as methane or derivatives thereof. Impurities and unwanted forms of carbon such as soot may be obtained in this manner; one of the causes may be the cracking of the gas in the space and away from the ceramic blanks. A similar procedure is used to make the so-called "boron-carbon" resistor which is accomplished by pyrolytic deposition of carbon and boron containing gases in the same type of batch flask.

This method of achieving a resistance coating by pyrolytic deposition is being used on a wider scale in the manufacture of resistors in spite of the fact that it is more time-consuming and expensive than other known methods of resistor manufacture. This is due in part at least to the more rigid standards which it is necessary to maintain because of the ever increasing complexity of design becoming common in various types of electronic development. Unfortunately, experience has proven that deposited carbon resistors made in these rotating flasks are often unstable, particularly when subjected to changes in humidity and load life, and it is often difficult to maintain desired resistance and temperature coefficient characteristics by such method. It is believed that this is due to the fact that the films formed on these ceramics by such rotating flasks are not uniformly hard and contain a number of impurities as well as carbon in a soft sooty form. Obviously any such conditions detract from the stability and required tolerance standards now in demand. Furthermore, the use of this method involving

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the rotating flask requires a relatively long time to form the required film, especially where low resistance values are needed.

It is an object of this invention to provide a method of and apparatus for pyrolytic deposition of carbon coatings on ceramics of the like which will be hard, uniform, free from impurities, and other forms of carbon such as soot. A further object is to provide apparatus for and a method of making this type of resistors much more quickly than has been done in the past without sacrificing but in fact markedly improving such important characteristics as the stability of the units so made. Other objects will be in part obvious and will in part be pointed out hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others and the apparatus embodying features of construction, combinations of elements, and arrangement of parts which are adapted to effect such steps, all as exemplified in the following detailed disclosure and the scope of the invention will be indicated in the claims to follow.

In the accompanying drawing in which are shown several possible embodiments of the above invention:

Figure 1 is a diagrammatic view of apparatus including a deposition flask which may be used in the practice of the method described herein;

Figure 2 is a perspective view of a ceramic blank on which a resistance coating has been applied by pyrolytic deposition;

Figure 3 is a perspective view of another modification of the deposition flask;

Figure 4 is a perspective view of another modification of the deposition flask;

Figure 5 is a perspective view of a further modification of the deposition flask;

Figure 6 is a longitudinal section view of a modification of the deposition flask shown in Figure 1 and related parts;

Figure 7 is a lateral sectional view taken along the lines 7—7 of Figure 6;

Figure 8 is a longitudinal sectional view of a further modification of the deposition flask shown in Figure 1 and related parts and

Figure 9 is a sectional view taken along the line 9—9 of Figure 8.

Similar reference characters refer to similar parts throughout the several views of the drawings.

Generally speaking I have discovered that by packing ceramic blanks closely together in a flask, heating the flask and introducing a carbon-containing gas such as methane, or a combination of methane with a boron-containing gas, that the resulting deposited coating on the ceramic will be hard, pure, free from sooty deposits and stable. Furthermore, the coating achieved in this manner has a desired uniform resistance characteristic throughout and these results are achieved without necessarily rotating the flask and at a much higher deposition speed than has been possible in the past. The apparatus for practicing this method may take a variety of forms as will be described in some detail hereinafter. Nevertheless, the fundamentals of this new method of pyrolytic deposition remain the same in each instance.

Turning now to Figure 1 of the drawings, the apparatus may comprise a flask 10 formed from refractory material such as quartz, having a closed end 10a, an open end 10b with a cover 11. A gas inlet tube 12 extends

through the cover 11 and along the central interior of flask 10 to a point substantially adjacent the closed end 10a thereof. The gases to be used may be supplied from tanks 18, 19, and 20 connected to the inlet tube 12 through valves 22 and meters 23. Flask 10 is placed in a suitable furnace 24 and is provided with a gas outlet tube 17 extending through cover 11.

In the practice of my method the closed end 10a of the flask is filled with a dummy load 13 of small ceramic granules, thus forming a porous layer surrounding the open end of inlet tube 12. Preferably these granules are of a size which will pass through 100 mesh screen although they may vary in size according to the size of the ceramic blanks to be coated. Next a charge 14 of ceramic blanks 15 which are to be coated with resistance material to form deposited carbon resistors are loaded adjacent dummy load 13. The ceramics 15, as shown in Figure 2, are usually cylindrical in shape and rather small in size. When they are loaded in the flask, care is taken to be sure that they are shaken together so that they occupy as little space as possible; no large spaces should be left between individual ceramics and such spaces must be fairly uniform in size. This may be accomplished without the use of any pressure; in fact it is best done by shaking the flask before it is inserted in the furnace so that the ceramics settle into a close mass. As so arranged the blanks 15 do not assume any particular order but the free spaces between individual blanks are quite small. Preferably, another dummy load 16 of ceramic granules is placed in the flask against the charge 14 of ceramics. This final load 16 of ceramic granules must be of sufficient size and weight to hold the ceramics 15 in the tightly compacted condition described above to assure that no spaces exist between such blanks 15 of any greater dimension than is necessary. Load 16 also serves to best seal charge 14 from the open end of the flask.

The flask 10 with its load, as described above, is then placed in furnace 24 where it is heated at least to the deposition temperature of the gases which are to be cracked and deposited by pyrolytic deposition on the ceramic blanks 15. While this heating is taking place and even after the deposition temperature has been achieved an inert gas such as nitrogen is passed through the flask via inlet tube 12 from tank 18 to flush out air and other impurities in the flask. It is to be understood that the flask will not only contain air as it is placed in the furnace which must be removed therefrom before deposition, but also the granules and ceramic blanks will have a certain amount of impurity on their surfaces which in large part is reduced to gaseous form during heating. The inert gas, such as nitrogen flushes these gaseous impurities out of the flask along with the air.

Illustratively, there is shown apparatus for making boron-carbon resistors in the embodiment of the invention now being described. Thus the tanks 19 and 20 are both connected to feed gas into the flask 10 by way of the inlet pipe 12. Tank 19 contains a hydrocarbon gas which may, for example, be methane, while tank 20 contains the boron gas and boron trichloride may be used for this purpose. After the flask has been thoroughly flushed by the inert gas, metered quantities of the deposition gases are fed into the flask from the tanks 19 and 20. After leaving the inlet tube 12 adjacent the closed end 10a of the flask the deposition gases are deflected thereby to flow back through the loads 13, 14 and 16 in the directions indicated by the arrows. The deposition gases are usually at room temperature when they enter the flask by way of pipe 12, but as they flow along the pipe inside the flask and as they flow back through the dummy load 13, they are heated and the temperatures and flow rates used are designed so that when the gases reach the charge 14 of ceramics they will have reached their deposition temperatures and, therefore, will crack on the surfaces of the ceramics to deposit by pyrolytic deposition a hard resistance coating

thereon. The deposition gases continue through the load of ceramics 14, as indicated by the arrows, and the cracking and pyrolytic deposition continues so that a coating or film of deposited material completely encases each ceramic. The deposition gases then pass through the dummy load 16 of granules and exit from the flask by way of outlet tube 17. A slight suction may be applied to the open end of the flask through tube 17 to achieve a more accurate control of the pyrolytic deposition although in practice it has been found that this is not essential. The dummy charge 16 not only acts to hold the load of ceramics in place but also as a heat buffer to protect the ceramics 15 from the cooler temperatures adjacent the open end 10b of the flask.

As noted above the ceramics 15 are carefully packed in the flask so that there is only a relatively small amount of free space between each individual ceramic; consequently cracking of the deposition gases takes place to a large extent on the surfaces of the ceramics. The best information available indicates that this is largely responsible for the hard deposit or coating achieved on the surfaces of the blanks. It is estimated that for best results the cross sectional area of the ceramic charge 14 in the flask during deposition should be made up of about equal parts of ceramic and space. Thus for a flask with a cross sectional area of 10 sq. centimeters, the space through which the gas flows would approximate 5 sq. centimeters. This total free space between the ceramic blanks during deposition determines the type of coating achieved and it has been found that if the blanks are of such size that there are five blanks per cubic centimeter in the flask or more, the spaces between the ceramics will be such as to provide a hard, uniform coating. However, if there are less than five ceramics per cubic centimeter such spaces will be too large as a rule and small granules should be mixed in with the ceramic charge to reduce the size of the spaces to that desired.

The hard coatings deposited on ceramic blanks by the method above described are far superior to those formerly achieved by deposition on a relatively small batch of ceramics where they are agitated in the large space of a rotating flask. It is surmised that this is due in part at least to the following phenomena: cracking of the deposition gases during pyrolytic deposition is caused by the molecules thereof colliding either with each other or with the ceramic blanks in the flask. When the blanks are packed closely together as in the present method the resulting small free spaces compel cracking of the majority of the molecules on the blanks instead of by collision in the free space. This cracking on the surface of the blanks at the deposition temperature achieves a hard coating as distinguished from a sooty deposit and also greatly increases the speed of deposition. On the other hand in flasks having large spaces unfilled with ceramics, a large portion of the gas is cracked by molecules colliding in such space with consequent formation of soot and other impurities and also a resulting limitation in the speed of deposition. Thus close packing as described eliminates a great deal of undesirable impurities which would otherwise be formed during the cracking; also such impurities as are necessarily formed are flushed out by the diluent inert gases which before and during deposition are passed through the free spaces between the ceramics rapidly so that a much more efficient flushing operation can be achieved.

In the practice of this method the relation of gas flow through the flask during deposition and temperature is of great importance. These relationships are best worked out via experiment for each type of deposition; flows and temperatures must obviously vary according to what deposition gases are used. The size of the ceramics, the particular type of material from which the ceramics are made, the type of coating desired on the ceramic, the resistance values to be achieved, the temperature coefficient characteristics wanted and a variety of other vari-

ables are all important factors. As an example, however, I have found that when using the method described above with respect to apparatus largely similar to that shown in Figure 1, I have achieved highly successful results when making boron-carbon resistors and using methane and boron trichloride with the following temperatures and flow-rates.

Furnace Temperature of—	Amount of Cold Gases Supplied to Flask, cc./min.	Approximate Speed of Gas through Flask, cc./sec.
2,200-----	7,000	100
2,150-----	3,600	50
1,900-----	400	5

Under some circumstances it may be desirable to rotate flask 10 very slowly, this depending largely upon the type of deposition being effected. This provides a slight agitation of the ceramics which is desirable. Surprisingly enough, however, I have found in practice that in most instances rotation of the flask is unnecessary, and that, in spite of the fact that the ceramics may touch each other during deposition, an even smooth uniform coating over the entire surface of the ceramic is achieved. Possibly this is partly due at least to the fact that in operation there is a very slight vibration of the flask not purposely imparted thereto but resulting from normal operation of the equipment, the usual vibrations found in a plant, etc. It is believed that this slight vibration, however, is not the most important factor. As has been explained above, the gases flow through the ceramic load rapidly in the practice of this method and such fast flow may lift the blanks apart where they touch sufficiently at least to allow for the desired deposition. Furthermore, while the blanks are touching at least part of the time it is believed that such points of contact are very small. It is known that ceramic blanks do not have a smooth surface but are pitted with hills and valleys. Thus when they contact only the tops of these hills are in engagement and these must be moved apart in the practice of this method because the result is an even deposition coating throughout the entire area of the ceramics when the method is completed.

The modified flask 25 shown in Figure 3 comprises a hollow substantially rectangular portion 26 which is relatively wide and thin with a neck portion 27 extending therefrom. Neck portion 27 is connected to an inlet tube, such as the tube 12 shown in Figure 1, and this flask may be used in the same manner as flask 10 in a furnace such as furnace 24. Flask 25 however is so shaped as to provide a large area of relatively small thickness and consequently all of the load of ceramics placed therein will be closer to the furnace; it is therefore possible to control the temperature of the ceramic load more accurately and to assure that it is uniform throughout the cross section of the load. This shape makes possible fast heating, even deposition temperatures, and consequently faster and more accurate all-around operation.

The modified flasks 29 and 31 shown in Figures 4 and 5 respectively are designed for the same purpose as the flask 25 of Figure 3. Thus flask 29 has four ribs 28 connected together in the form of an X with a tubular neck portion 30 connected to an inlet tube, such as tube 12 in Figure 1. Flask 31 is very similar to flask 29 except that it has three ribs 28 in the shape of a Y and a neck portion 32 which may be connected to a gas inlet tube. The shapes of the flasks 29 and 31 are admirably suited to provide a large area where a load of ceramics having a relatively small thickness may be packed to achieve the desirable results mentioned with respect to flask 25 in Figure 2.

In the operation of the flask shown in Figure 1 the resistance of the individual ceramic blanks is dependent upon the distance of such blanks from the first point of

pyrolytic deposition. More specifically, still referring to Figure 1, the ceramic blanks 15 in charge 14 adjacent the dummy load 13 will be subject to greater deposition and hence contain thicker coatings than the coatings on the ceramic blanks further back in the load. It can be said as a general proposition that the further away the blanks are from the initial point of deposition, the thinner the resultant deposited coating will be. Inasmuch as the resistance value of the blank 15 is inversely proportional to the thickness of the coating it can also be stated that the resistance values in the charge 14 vary inversely as distance increases from the point of original pyrolytic deposition. In the usual circumstance this is not an important difficulty inasmuch as in manufacturing processes resistances having a variety of resistance values are desired. Temperatures and flow rates can be so worked out that the variations in resistance value throughout the charge will not be unduly marked and the blanks will be sufficiently coated to have usable resistance values.

Where, however, it is more important to maintain substantially uniform resistance values throughout the charge of ceramic blanks resort may be had to the embodiment of my invention shown in Figure 6. In this embodiment a flask 10 similar to the flask in Figure 1 described above may be utilized, and an inlet pipe 33 has a horizontal portion 33a extending along and spaced immediately above the bottom of the flask, as it is arranged in the furnace after loading and when being readied for deposition. The inner end of the tube 33 has a right angle portion including the vertical section 33b and a horizontal section terminating in the opening 33c. A portion of the horizontal length 33a of the tube has a longitudinal slot formed therein facing the bottom 10c of the flask and extending substantially from the points x and y on the horizontal length 33b. Thus as can be understood from a consideration of Figures 6 and 7 the longitudinal slot 33d does not extend throughout the entire length of flask 10 and is in fact positioned to be positioned immediately beneath the charge of ceramics to be coated, as will be described in detail now.

Still referring to Figures 6 and 7, a dummy load of ceramic granules 34 is first longitudinally disposed along the bottom of the flask 10 to cover section 33a of the tube 33 and to provide a floor for the charge of ceramics 35 which rests thereabove. The ceramics are packed in tightly to allow for as little space therebetween as possible, as has been described in detail with respect to the embodiment of the invention shown in Figure 1. A free space 36 remains above the charge of ceramics 35, as can be seen in Figures 6 and 7, and interposed between the charge and the open end of the flask is a vertically disposed dummy load 37 of ceramic granules to seal off or provide a heat shield from the atmosphere.

After the flask is placed in a furnace loaded as described above and in the position shown in Figures 6 and 7, it is heated in the usual manner to bring it up to the required deposition temperature after which the deposition gases are introduced by way of the tube 33 as has previously been described in detail. The great majority of the deposition gases flow out substantially in circumferential and diametric directions from the slot 33d, as indicated by the arrows in Figures 6 and 7. More particularly the flow deposition gases from the slot 33d is in more or less vertical directions as viewed in Figure 7 through the dummy load of ceramic granules 34 at the bottom of the flask and thence, as the gases reach deposition temperature, through the ceramic load and upwardly into the free space. Some of the gas, i. e. the deposition gas, continues on through the tube and exits into the space 36 from the open end 33c of the tube where it picks up the gases which have passed through the charge 35 and flows out of the flask through granules 37. It will now be understood that because the gases pass merely from the slot 10d and through the relatively short path from the top of the dummy load 34 to the space 36 during deposition, cracking and depositing take place in a very short time and

during a very short linear travel. Consequently, variation in resistance coating and resistance value in the blanks located adjacent the dummy load 34 and those adjacent the free space 36 is small. In this manner, it is possible to achieve great uniformity of resultant produce and it will be obvious that the thinner the layer 36 of ceramic the more uniform will be the resistance values to be achieved by this embodiment of my invention.

In the embodiment of the invention shown in Figures 8 and 9 the flask 10 has a gas inlet tube 40 and an outlet tube 41. Inlet tube 40 extends along the bottom of the flask as viewed in these figures and terminates in a closed end 40a; it is provided with a longitudinal slot 40b facing the flask as can be seen in Figure 8. The outlet tube 41 substantially similar in construction to tube 40, is disposed at the top of the flask, as shown in Figures 8 and 9 having a closed end 41a and a longitudinal slot 41b similar to slot 40b and also facing the flask. A heat buffer 43 is disposed at the open end of the flask comprising the rod 43a having flanges 43b disposed at its opposite ends. Flanges 43a and 43b have formed therein notches 43c to receive the tubes 40 and 41 as can be seen in Figure 9.

In operation this flask is loaded with blanks packed therein in random fashion and after heating and flushing in a furnace, deposition gases are introduced through the tube 40 in the usual manner. A slight suction is applied to the outlet tube 41 and consequently the gases flow from the slot 40b substantially upwardly and diametrically through the load, as indicated by the arrows in Figures 8 and 9, to be drawn into the longitudinal slot 41b and then withdrawn from the flask by way of the tube 41. With this apparatus, a relatively large load of ceramics may be coated by pyrolytic deposition at one time and the apparatus is particularly suited for rotation in a furnace by suitable apparatus well known in the art.

It is well known in the art that pyrolytic deposition of a resistance coating may be accomplished on a variety of materials although it is usually done on various types of ceramics all depending on the results desired. However, this invention is not limited to the particular type of material used for the blanks and therefore it is intended that wherever the expressions "ceramics" or "ceramic blanks" are used in the specification or claims it is to be construed as meaning any suitable dielectric material capable of withstanding the deposition temperatures necessary to effect the desired pyrolytic deposition.

While pyrolytic deposition to achieve resistance coatings on ceramic blanks has usually been accomplished with carbon or boron containing gases or mixtures thereof, such as, for example, a hydrocarbon or a boron chloride, the invention herein is not limited to the particular type of deposition gas used. Therefore, the expression "deposition gas" as used herein is intended to signify any gas capable of cracking at a deposition temperature to deposit a hard coating on a ceramic blank by pyrolysis. It follows that wherever the expression "deposition temperature" is used in the specification or claims, it is intended to mean the temperature best suited to crack the gas or gases being used to thereby effect pyrolytic deposition.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the constructions set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

I claim:

1. In a method of coating a ceramic blank with a resistance material by pyrolytic deposition, the steps of packing a mass of ceramic blanks in indiscriminate random relatively contacting fashion with substantially a minimum total space therebetween by shaking them to form a closely packed mass, passing a gaseous mixture through such mass while maintaining said mass in the relative packed condition, said mixture comprising an inert gas and a deposition gas which will crack upon heating to a deposition temperature, and heating said mass to said deposition temperature to deposit by pyrolysis a hard resistance coating on each blank.

2. In a method of coating a ceramic blank with a resistance material by pyrolytic deposition, the steps of packing a mass of ceramic blanks in indiscriminate random relatively contacting fashion with substantially a minimum space therebetween by shaking them to form a closely packed mass while maintaining said mass in the relative packed condition, passing a gaseous mixture through said mass, said mixture comprising an inert gas and a deposition gas of such composition as to deposit a hard carbon coating on said blank by pyrolytic deposition upon heating to a deposition temperature, and heating said mass to said deposition temperature to deposit by pyrolysis a hard resistance coating on each blank, said blanks being packed close enough together so that the space therebetween is not large enough to permit any substantial cracking of gas therein whereby most of the material resulting from pyrolytic cracking of the deposition gas deposits directly on said blanks from cracking occurring on the surface thereof.

3. The method defined in claim 2 in which the spaces between the blanks are small enough to permit a rapid flow of the gas therethrough while still effecting pyrolytic deposition of a coating of resistance material on such blanks.

4. In a method of coating a ceramic blank with a resistance material by pyrolytic deposition, the steps of packing a charge of ceramic blanks in indiscriminate random relatively contacting fashion closely by shaking them together, packing a dummy load of ceramic granules across the exposed surfaces of said charge to act as a heat shield from the atmosphere, passing a gaseous mixture through said dummy load of ceramic granules and then substantially evenly through said charge of ceramic blanks while maintaining said charge in the relative packed condition, said mixture comprising a deposition gas capable of cracking upon being heated to a deposition temperature, and heating said charge and said deposition gas to deposit a hard uniform resistance coating on each blank.

5. The method defined in claim 4 in which the deposition gas is heated to the deposition temperature of the deposition gas being used prior to being passed through said charge of blanks.

6. The method defined in claim 4 in which said mass of granules is heated to the deposition temperature or thereabove, and a deposition gas is passed through said mass to heat it to said temperature prior to passage through said charge of blanks.

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